

Title: Fractionation and Separation of Polydisperse Nanoparticle Populations into Distinct Monodisperse Fractions using CO₂ gas expanded liquids

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OBJECTIVES: The size dependent properties of nanoscale materials allows them to be engineered to have specific functions such as in catalysts, quantum dots for optical properties, size dependent conduction of electrons in Ag nanoparticles and in the production of high quality ordered arrays and ordered thin films. While solution based nanoparticle formation techniques are attractive due to their simplicity, they often result in synthesis of particles with a wide size range (e.g. 1 to 20 nm). As such, post synthesis processing is required to further refine the size distribution to the desired monodisperse range. A variety of post-synthesis techniques have been developed to narrow size distributions including the use of liquid antisolvents to selectively control precipitation, isoelectric focusing electrophoresis (IEF) and chromatography techniques. Addition of liquid antisolvent such as ethanol is the most commonly used method to cause size selective nanoparticle precipitation from organic solution. But in addition to being time consuming and solvent intensive, the technique can be subjective as it is often based on the observed opalescence of the solution upon antisolvent addition. This project presents a process for rapid and precise size separation of polydisperse nanoparticle populations into monodisperse fractions using the pressure tunable physico-chemical properties of CO₂ gas expanded liquid (GEL) solutions where CO₂ acts as an antisolvent (*Nanoletters*, 5, 461, 2005). To improve our fundamental understanding and to refine the size separation process, this study is being performed to identify the key parameters enabling size separation of various nanoparticle populations.

ACCOMPLISHMENTS TO DATE: This work utilizes highly tunable solvent properties of organic/CO₂ solvent mixtures to selectively precipitate and size separate dispersions of polydisperse metal nanoparticles (2 to 12 nm) in organic solvent into multiple, monodisperse fractions (± 0.5 nm). A novel high pressure apparatus that confines the particle precipitation to a specified location on a surface was fabricated as shown in Figure. The dispersibility of the ligand-stabilized nanoparticles was controlled by altering the ligand-solvent interaction (solvation) through the addition of the CO₂ gas as an antisolvent, thereby tailoring the bulk solvent strength. As such, the solvent interaction with the ligand tails was diminished to a value below a threshold interaction energy necessary for dispersion of particles of a given size. Below this solvent strength, particles of that size or larger precipitated. Therefore, the solvent strength of the medium was tuned through CO₂ pressurization to provide sequential precipitation of increasingly smaller particles in a simple, controllable process. Compared to current techniques, this CO₂ expanded liquid approach provides for faster and more efficient particle size separation, reduction in organic solvent usage, and pressure tunable size selection in a single process. This study details the influence of various factors on the size separation process, such as the types of metal nanoparticles, ligand type and solvent type as well as the use of recursive fractionation and the time allowed for settling during each fractionation step (*J. Phys. Chem. B* (2005), 109(48), 22852). This size separation process was successfully employed for the separation of both Ag and Au nanoparticles. The pressure range required for the precipitation process in hexane solvent is the same for both the silver and gold particles capped with dodecanethiol ligands. This is consistent with the fact that both dodecanethiol stabilized gold and dodecanethiol stabilized silver nanoparticles have Hamaker

constants of 1.95eV resulting in similar inherent van der Waals forces that impact precipitation at a given solvent strength.

The influence of thiol chain length, from hexanethiol to tetradecanethiol, was investigated on the size- separation process. This range was chosen because thiol chain lengths smaller than hexa and greater than tetradeca can not stabilize the particle dispersion for long periods of time. Our results suggest that dodecanethiol ligands provide the optimum length for strong ligand – solvent interactions. The effect of different solvents on the size selective precipitation and fractionation process was also examined. In hexane, a large percentage of the particles remained dispersed up to 550 psi after which point more appreciable precipitation occurred (precipitation of successively smaller particles) with further increases in CO₂ pressure until all the particles had precipitated at 700 psi.

In contrast to hexane, pentane is a slightly weaker solvent, and as such, appreciable precipitation was initiated at only 450 psi with complete precipitation as low as 600 psi. Given that pentane provides weaker solvation of the ligand tails than hexane, smaller amounts of CO₂ are necessary to bring the solvent/CO₂ mixture solvent strength below the threshold for dispersability of a given particle size. As a result, the pressure range required for precipitation is less in pentane than hexane. Interestingly, heptane and octane both exhibit stronger interactions with the ligand tails as compared to hexane resulting in more stable dispersions in the longer chain length solvents. Correspondingly, greater CO₂ pressure is required to reach the same weakened solvent strength of the solvent/CO₂ mixture to induce precipitation of nanoparticles of a given size. The length of the organic solvent influences the gold nanoparticle precipitation process where the longer length solvent molecules have stronger interactions with the nanoparticle ligand tails compared to the shorter length solvent molecules. Additional results of similar experiments performed with cyclohexane, decane, isooctane, and toluene shows that in these solvent systems, particle dispersability remained quite high even at CO₂ pressures approaching the vapor pressure of CO₂ where the dodecanethiol coated gold particles remained dispersed in the solvent/CO₂ mixtures for several hours. Temperature is another variable that impacts the dispersibility of the nanoparticles through changes in the density and the mole fraction of CO₂ in the gas expanded liquids. At 22 °C, the nanoparticle precipitation occurs between 500 and 700 psi CO₂ pressure. At 35 °C, this pressure range for precipitation was shifted up to 650 to 800 psi, illustrating that an increase in pressure is required for precipitation with an increase in temperature. This variation is due in part to the CO₂ density change with temperature. As temperature is increased, the mole fraction of CO₂ in the organic liquid/CO₂ mixture is reduced resulting in a smaller volume expansion of the liquid dispersion at a given pressure. This, therefore, reduces the antisolvent effect in the nanoparticle precipitation.

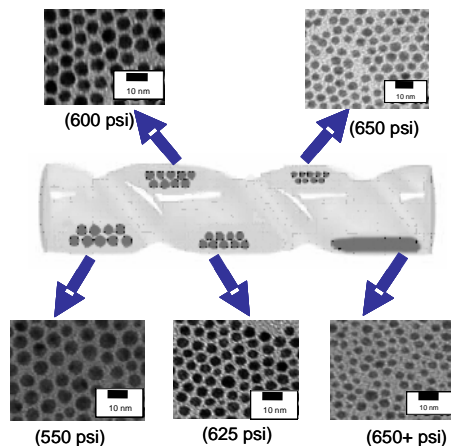


Figure: TEM images of dodecanethiol-coated gold particles fractionated with the CO₂ expanded liquid technique in the range of 550 psi to 650+ psi.

FUTURE WORK: Future work on this project will involve three primary tasks including:

Task 1: Identify the key properties enabling separating multiple nanoparticle populations to within a standard deviation of 1nm. In addition to continuing our investigations of the effects described above, we will also investigate the effect of holding time during each successive fractionation as well as the effect of repeating a set of size separation experiments on one of the recovered fractions to further improve the size separation process using CO₂ as an antisolvent.

Task 2: Apply the general procedure developed for Ag nanoparticles to other common nanoparticles such as CdSe quantum dots, Pt, Pd, while maintaining a standard deviation of 1 nm.

Task 3: Process samples > 1g achieving mono-disperse metal catalyst nanoparticles with a standard deviation of 1nm.

PUBLICATIONS

- M. Anand, P. W. Bell, C. B. Roberts, "Synthesis and Stearic Stabilization of Silver Nanoparticles in Carbon dioxide Using Fluorine-Free Compounds," *J. Phys. Chem. B* (Submitted).
- J. Liu, M. Anand, C. B. Roberts, "Synthesis and Extraction of β -D glucose Stabilized Au Nanoparticles Processed into Low Defect, Wide Area Thin Films And Ordered Arrays Using CO₂-Expanded Liquids," *Langmuir* (2006), ASAP Article.
- M. Anand, M. C. McLeod, P. W. Bell, C. B. Roberts, "Tunable Solvation Effects on the Size-Selective Fractionation of Metal Nanoparticles in CO₂ Gas-Expanded Solvents," *J. Phys. Chem. B* (2005), 109(48), 22852-22859. (The paper was prepared after this proposal was submitted, but before the official project start date).

PRESENTATIONS

- Anand, M., Bell, P. W., Roberts, C. B., "Benign process for Silver nanoparticles synthesis and processing in neat Carbon dioxide solvent using Fluorine-free compounds," *10th Annual Green Chemistry and Engineering Conference*, Washington, DC, June 26-30, 2006
- Liu, J., Anand, M., Roberts, C. B., "Synthesis and Extraction of β -D glucose Stabilized Au Nanoparticles Processed into Low Defect, Wide Area Thin Films And Ordered Arrays Using CO₂-Expanded Liquids," *10th Annual Green Chemistry and Engineering Conference*, Washington, DC, June 26-30, 2006
- Roberts, C.B., Anand, M., Liu, J., Bell, P.W., "Metallic nanoparticle deposition and separation using CO₂-expanded liquids and supercritical CO₂ processing", *Invited seminar*, Georgia Institute of Technology, Department of Chemical Engineering, April 5, 2006.
- Roberts, C.B., Anand, M., Liu, J., "Metallic nanoparticle deposition and separation using CO₂-expanded liquids and supercritical CO₂ processing", *Invited seminar*, Tennessee Technical University, Department of Chemical Engineering, March 30, 2006.
- Anand, M., Bell, P. W., Liu, J., Roberts, C. B., "Size selective fractionation of nanoparticles using the tunable solvent properties of CO₂ gas expanded liquids," *AIChE 2005 Annual Meeting*, Cincinnati. (The presentation was made after this proposal was submitted, but before the official project start date).

STUDENTS SUPPORTED UNDER THIS GRANT –

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